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ORIGINAL RESERACH

Effects of $SrTiO_3$ buffer layer on structural and electrical properties of $Bi_{3.15}Nd_{0.85}Ti_3O_{12}$ thin films prepared by a chemical method

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Abstract Ferroelectric $Bi_{3.15}Nd_{0.85}Ti_3O_{12}$ (BNT) thin films have been grown on $Pt/Ti/SiO_2/Si$ substrates at 750 °C by a chemical solution deposition method using $SrTiO_3$ (STO) as a buffer layer. The influence of STO buffer layer on the phase and microstructure of BNT thin films was examined by X-ray diffraction (XRD) and scanning electron microscopy (SEM). The electrical properties were investigated both for BNT thin films with and without STO buffer layer. The results showed that STO buffer layer strongly influenced the microstructure and electric properties of BNT thin films. BNT ferroelectric thin films with STO buffer layer exhibited the good crystallization behavior, the enhanced fatigue characteristics and excellent leakage current properties. This indicates that the introduction of the STO buffer layer prevents the interfacial diffusion and charge injection between BNT thin films and the substrate effectively and improves the interface quality.

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1. Introduction

Ferroelectric thin films have aroused researchers' great interest for the potential applications in nonvolatile ferroelectric random access memories (NvFeRAMs) because of their high speed, low consumption, nonvolatility, radiant hardness, and overall robustness [1,2]. $Bi_{3.15}Nd_{0.85}Ti_3O_{12}$ (BNT), one of bismuth-layer-structured ferroelectrics, has attracted a great deal of attention as a candidate memory media for NvFeRAMs applications due to its lead-free chemical composition, relatively large remnant polarization, good fatigue resistance, low processing temperature and high Curie temperature [3–8]. However, ferroelectric materials suffer from the degradation

in the electrical properties owing to interfacial effects, including either the finite screening length of the bound polarization charge [9–11], an intrinsic dead layer at the interface [12–14], space charge effects [15], or residual stresses induced by the lattice mismatch and thermal misfit [16,17], and the charged defects like oxygen vacancies [18,19]. Many attempts have been made to enhance the properties of the ferroelectric films, such as the control of heat treatment condition, the insertion of a buffer layer and the choice of different bottom electrodes [20–22]. It has been shown that the introduction of a buffer layer such as $SrRuO_3$, $La_{0.5}Sr_{0.5}CoO_3$, $La_{0.7}Sr_{0.3}MnO_3$, $YBa_2Cu_3O_{7-x}$, $LaNiO_3$, MgO, ZnO and $SrTiO_3$ (STO), is an effective method to improve fatigue and retention characteristics of these ferroelectric thin films for memory application [23–31]. Up to now, there have been few reports about introducing STO buffer layers between BNT thin films and $Pt/Ti/SiO_2/Si$ (100) substrates. STO has a cubic perovskite structure and relatively high dielectric constant compared to BNT [32]. In addition, the lattice parameter of STO is 0.390 nm, which is close to that of Pt (0.392 nm). The similarities in the crystal structures and lattice constants provide favorable conditions of better lattice match and structural compatibility for improving electric properties of BNT thin film.

In this work Pt/BNT/Pt, Pt/BNT/STO/Pt and Pt/STO/BNT/STO/Pt capacitors were prepared for comparable study. The influences of buffer layer on the structure and electric properties of BNT thin films were examined. The possible reason resulting in the change of electric behavior was discussed.

2. Experimental

The BNT thin films were fabricated by dissolving bismuth nitrate, neodymium nitrate, and titanium butoxide in proportion in glacial acetic and 2-methoxyethanol at room temperature, with appropriate amount of acetylacetone added to stabilize the solution. 10% excess of bismuth nitrate was added to compensate for possible bismuth loss during the thermal annealing process. The final concentration of precursor solution was adjusted to 0.1 M. The final concentration of STO precursor solution was adjusted to 0.05 M, using strontium acetate and titanium butoxide as start material sources and glacial acetic, 2-methoxyethanol and acetylacetone as solvent and stabilizing agent, respectively. The above two mixtures were both stirred for 12 h and then kept for 1 week to obtain the desired solutions. The thin film was deposited using a repeated coating/drying cycle. Firstly, a thin STO buffer layer was spin-coated onto $Pt/Ti/SiO_2/Si$ substrate. The films was dried at 180 °C for 5 min, prefired at 400 °C for 5 min to remove residual organic compounds and annealed at 750 °C for 30 min in a rapid thermal annealing (RTA) furnace in O_2 ambient. Then the BNT layer was repeatedly deposited on the STO layer with the same process to achieve desired film thickness. The coated BNT films were also annealed at 750 °C for 30 min in O_2 ambient by a RTA process. And the films finally reached the thickness of about 450 nm.

The crystal structure and crystalline orientation of the prepared films were studied using a D/max 2500 X-ray diffractometer with Cu Kα radiation. The surface morphologies of the prepared films were characterized by scanning electron microscope (SEM). For electrical measurements, Pt top electrodes were fabricated on the BNT thin films by direct current sputtering through a shadow mask. The ferroelectric and fatigue characteristics were measured using a Radiant Technologies Precision Workstation ferroelectric tester system. The leakage current properties were tested by a precision semiconductor parameter analyzer Agilent 4156C with a micrometer probe station.

3. Results and discussion

Fig. 1 shows the XRD patterns of BNT films with and without STO buffer layer. The X-ray patterns indicate that all the films are typical perovskite and polycrystalline structure and show the (00*l*) and (117) peaks in the XRD spectra. It can be found that BNT films with STO buffer layer did not induce other second phases, this indicates that the introduction of STO buffer layer cannot affect the crystal orientation of the BNT film.

The surface morphologies of the films are presented in Fig. 2(a)–(c). The surface of the BNT films without STO buffer layer was rough and inhomogeneous, and some pin-holes and micro-cracks were found in the grain boundaries, as shown in Fig. 2(a). By adding STO buffer layer (Fig. 2(b) and (c)), the film surface became very smooth and uniform, the pin-holes and micro-cracks disappeared. It was clearly seen that BNT films with STO buffer layer showed much denser microstructure than BNT films deposited directly on Pt substrates, this may be attributed to the different interaction strength between the substrates and the deposited atoms, and the different lattice mismatch between the substrates and BNT thin films, which directly influences the nucleation and growth dynamics. This result suggests that the STO buffer layer substantially improves the crystallization behavior and the microstructure of BNT thin films.

Fig. 3(a) shows the hysteresis loops of various BNT capacitors annealed at 750 °C for 30 min in oxygen ambient. It was found that all BNT capacitors showed well-saturated hysteresis loops. However, the values of remanent polarization (P_r) of BNT films with STO buffer layer were improved significantly in comparison with those without STO buffer

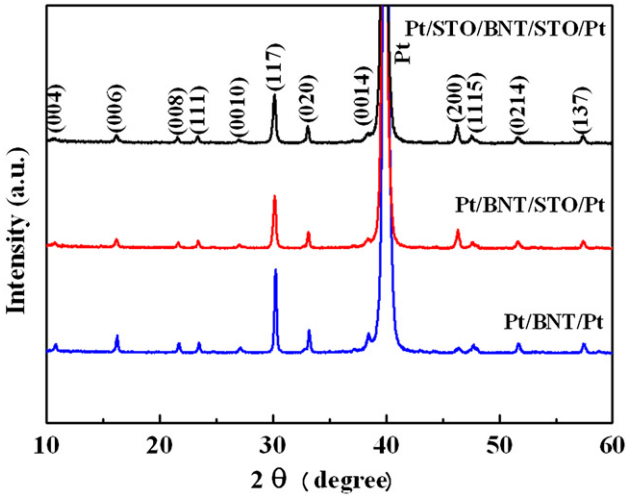

Fig. 1 XRD patterns of BNT films with and without STO buffer layer.

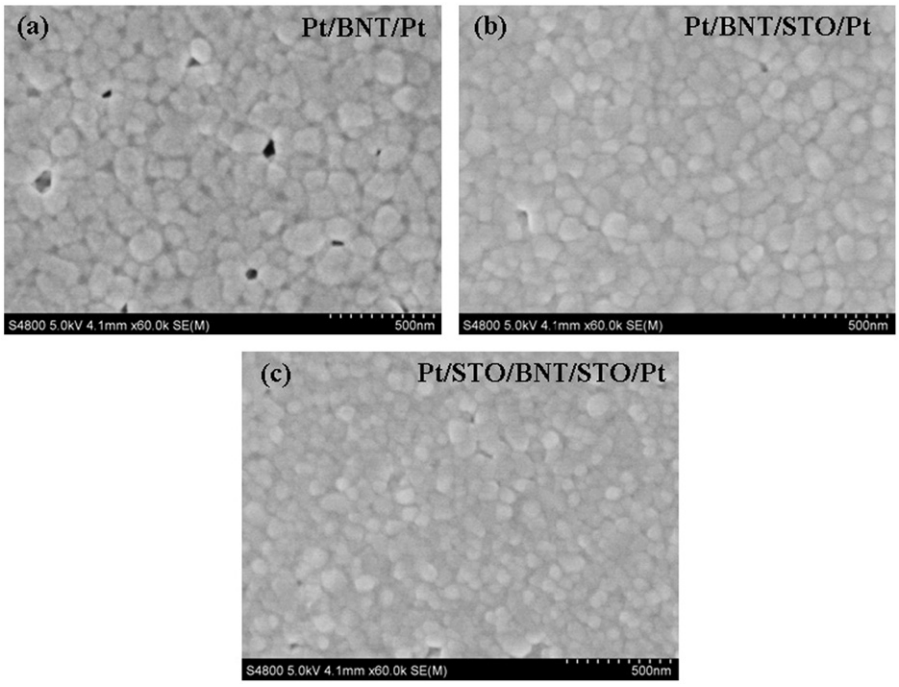

Fig. 2 Surface morphologies of BNT films with and without STO buffer layer.

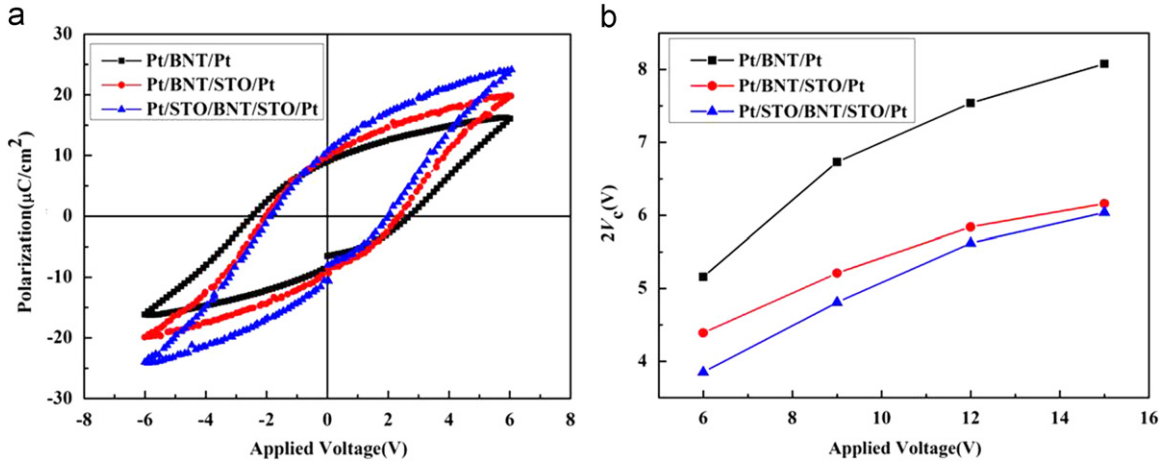

Fig. 3 (a) Hysteresis loops of various BNT capacitors. (b) $2V_c$ values of various BNT capacitors.

layer. At the applied voltage of 6 V, the $2P_r$ value for the Pt/BNT/Pt capacitor was 17.32 μC/cm^2. But the $2P_r$ values for Pt/BNT/STO/Pt and Pt/STO/BNT/STO/Pt capacitors measured at the same applied voltage were increased to 19.18 μC/cm^2 and 21.40 μC/cm^2, respectively. This may be ascribed to the good crystallization behavior of the thin films and the suppression of bismuth loss at the interface due to the introduction of STO buffer layer [33]. Fig. 3(b) displays the variation in the values of the coercive voltage (V_c) of the various BNT capacitors with the applied voltage. It was observed that the values of $2V_c$ increased with the increase of the applied voltage. The $2V_c$ values of the BNT films with STO buffer layer were much smaller than that of BNT films deposited directly on Pt. The $2V_c$ value for Pt/BNT/Pt capacitor was 8.08 V at the applied voltage of 15 V. When the STO buffer layer was employed, the $2V_c$ values reduced to 6.16 V and 6.04 V for Pt/BNT/STO/Pt and Pt/STO/BNT/STO/Pt capacitors, respectively. The coercive voltage of BNT thin films was controlled by such factors as the space-charge, domain pinning by defects, orientation, sample thickness, etc. [15,34,35]. In order to avoid the influence of sample thickness, we prepared the BNT thin films of the same thickness for every capacitor. The reduction of the coercive voltage could also exclude the orientation effect, since the orientation of BNT thin films almost remained unchanged from the results of XRD, when the STO buffer layer was used. Therefore, the origins of the lower coercive field in the BNT films can perhaps be considered as follows. When inserting additional STO buffer layer, the crystallization behavior of the BNT films and the interface quality between BNT and Pt improved, the space-charge layer near the crystal surface and the vacancy could be suppressed, and the domain pinning was eliminated effectively. These may be the main factors that lead to the reduction of the coercive voltage in BNT films with STO buffer layer.

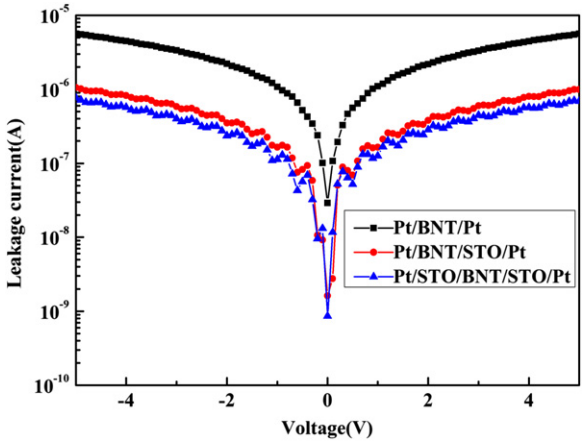

Fig. 4 Leakage current characteristics of BNT films with and without STO buffer layer.

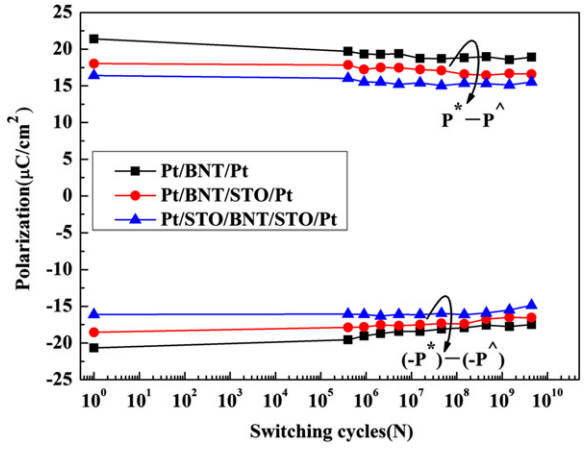

Fig. 5 Fatigue characteristics of various BNT capacitors.

Leakage current characteristics of BNT films with and without STO buffer layer were measured at room temperature, and the results are shown in Fig. 4. It can be seen that the leakage current of BNT films without STO buffer layer films was about 5×10^{-6} A with a positive applied voltage up to 5 V. However the introduction of STO buffer layer displayed a sharp decrease of the leakage curve. The leakage currents for Pt/BNT/STO/Pt and Pt/STO/BNT/STO/Pt capacitors reduced to 9×10^{-7} A and 6×10^{-7} A, respectively. The reduced leakage current of the BNT film may be attributed to the effective improvement in the interface quality by the STO buffer layer [36]. It is known that the microstructure in the vicinity of the film/substrate interface plays an important role in defining the leakage current in films. As an excellent isolating material, the STO buffer layer can effectively suppress the interdiffusion and charge injection between BNT and Pt [31]. Therefore, the interface between BNT and Pt is improved by inserting STO as buffer layer, and the leakage situation is obviously modified.

Fig. 5 presents the fatigue characteristics of various BNT capacitors annealed at 750 °C for 30 min in oxygen ambient. The fatigue test was performed at room temperature using 5 V bipolar square pulses and a frequency of 100 kHz. P^*, $\hat{P}$,-P^* and -$\hat{P}$ represent switched polarization, nonswitched polarization, the opposite-state switched and nonswitched polarization, separately. As shown in Fig. 5, both (P^*–$\hat{P}$) and [(-P^*)–(-$\hat{P}$)], which are practically the most important parameters to evaluate the FeRAM devices, decreased with increasing switching cycles in all BNT capacitors. However, it can be seen that [(-P^*)–(-$\hat{P}$)] decreased much faster than (P^*–$\hat{P}$). The losses were 15.4% and 11.7% respectively for Pt/BNT/Pt capacitor after the sample was switched up 4.45×10^9 cycles. This result indicates that the opposite-state polarization fatigue is a much more serious issue for practical applications. In contrast to the BNT directly on Pt, there was no obvious polarization degradation in BNT films with STO buffer layer. The degradation rates of 7.9% and 10.8% for the same- and the opposite-state in Pt/BNT/STO/Pt capacitor structure were observed after 4.45×10^9 cycles, which were much slower than that for BNT directly on Pt. For Pt/STO/BNT/STO/Pt capacitor, even less changes (5.4% and 7.8%) in polarization values were detected. Therefore, it is ascertained that the use of STO buffer layer improves the fatigue characteristics of BNT thin films.

4. Conclusions

STO buffered BNT ferroelectric thin films were prepared, and the structure and electric properties of BNT thin films were obviously improved. This may be attributed to the good interface quality by adding STO buffer layer. The experimental results showed that the values of $2P_r$ increased from 17.32 μC/cm^2 to 21.40 μC/cm^2 while the values of $2V_c$ were significantly decreased. The leakage situation and the fatigue characteristics were also obviously modified by adding STO buffer layer.

Acknowledgments

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